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INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2001B133	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 02/11407	International filing date (day/month/year) 11.10.2002	Priority date (day/month/year) 16.10.2001
International Patent Classification (IPC) or both national classification and IPC C07C1/00		
Applicant EXXONMOBIL CHEMICAL PATENTS INC. et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 21 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the opinion</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>		
Date of submission of the demand  18.04.2003	Date of completion of this report  16.01.04	
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Jardon Alvarez, J  Telephone No. +49 89 2399-8325  	

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP 02/11407

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

13 as originally filed  
1, 1A, 2, 2A, 3, 4, 5, 6, 6A, 7, filed with telefax on 26.10.2003  
7A, 8, 9, 9A, 10, 11, 12, 14

**Claims, Numbers**

1-15 filed with telefax on 26.10.2003

**Drawings, Sheets**

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 02/11407**

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:
- ☐ the entire international application,
  - ☒ claims Nos. 7-15  
because:
    - ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):
    - ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
    - ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
    - ☒ no international search report has been established for the said claims Nos. 7-15.
2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:
- ☐ the written form has not been furnished or does not comply with the Standard.
  - ☐ the computer readable form has not been furnished or does not comply with the Standard.

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-6
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-6
Industrial applicability (IA)	Yes: Claims	1-6
	No: Claims	

2. Citations and explanations

**see separate sheet**

**Re Item III**

**Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

1. Claims 7 to 15 were filed after the establishment of the International Search Report. These claims relate to a multi step process for producing olefins from methanol which was not covered by the original claims. A report cannot be established for this subject-matter because it has not been searched and no time was left after the filing date to allow an additional search.

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

D1: US - 4 387 263  
D2: US - 4 547 602  
D3: US - 4 560 537  
D4: EP - A - 0 060 103

1. None of the available documents discloses a method for processing an olefin stream containing oxygenates and water including the **two steps washing of the olefin stream** with first methanol to remove at least a portion of the oxygenate from the olefin stream and then with water as claimed in claims 1 to 6.

Documents D1 and D4 disclose closely related process but in the process of D1 the washing is made only with water (see Fig. 1) and in the process of D4 the washing is made only with methanol (see Fig. 1/1). In documents D2 and D3 no washing step of the effluent stream is mentioned.

The subject-matter of claims 1 to 6 is then novel (Art. 33(2) PCT).

2. However the subject-matter of claims 1 to 6 does not involve an inventive step as required by Article 33(3) PCT.
  - 2.1. As pointed out above documents D1 and D4 disclose closely related methods for the treatment of olefin streams containing oxygenates. The problem to be solved

by the present application can be seen as to find additional methods to more easily remove oxygenates from olefins (see page 1, last three lines of the present description).

- 2.2. This problem is solved by the process of claim 1 including the washing of the olefin stream with methanol and contacting the methanol washed olefin stream with water. By these measures undesirable oxygenates from an olefin stream are said to be removed.
- 2.3. Having regard to the fact that D1 and D4 already disclose the beneficial use of methanol or water to remove oxygenates such as dimethyl ether it would appear obvious to combine the teaching of both documents and thus arrive at the process now claimed. In the absence of an unexpected effect for the combination of these known measures an inventive step cannot be acknowledged.
- 2.4. It has been argued by the applicant in his letter dated October 26, 2003 that the two steps washing results in a more effective removal of oxygenated byproducts and unreacted feed than the prior art processes using only water or only methanol. However the present application does not contain any experimental evidence in support of such statement and therefore this argument cannot be considered in support of inventive step. It has further been argued by the applicant that the use of a specific methanol range; results in improved removal of oxygenates but claims 1 to 6 are not limited to such a range.

Consequently the applicant's arguments cannot support the existence of an inventive step for the claimed subject-matter.

## A METHOD FOR PROCESSING AN OLEFIN-CONTAINING PRODUCT STREAM

[0001] This application claims benefit of the filing date of German Patent Application No. 101 50 480.2, filed October 16, 2001.

### Field of the Invention

[0002] This invention concerns a method for processing an olefin-containing product stream that contains, besides ethylene and propylene, longer chain olefins and compounds of hydrocarbons with oxygen (oxygenates), where the product stream is dewatered in successive process steps, optionally compressed in several steps and dried, and then sent to fractionation.

### Background of the Invention

[0003] Producing olefins from methanol have been considered an interesting alternative to the traditional production of olefins from petroleum. Methanol is considered to be a readily stored and managed intermediate product for utilization of hitherto unused natural gas. Thus, the increasing demands for olefins on the world market could also be served by using very cheap methane. For this reason, processes are being developed that produce short-chain olefins from methanol. Such processes operate, for example, catalytically according to the overall equation  $2\text{CH}_3\text{OH} \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$ . Besides the desired olefins, ethylene and propylene, longer-chain olefins and, especially, undesired compounds of hydrocarbons with oxygen (oxygenates) such as alcohols, ketones and organic acids also form. For this reason a costly secondary purification of the reaction product is necessary. One oxygenate that is particularly to be taken into account is dimethyl ether (DME), since it is one of the lightest oxygenates and behaves similarly to  $\text{C}_3$  in distillation processes. Moreover, it is only slightly polar, so it can be difficult to remove by absorption. Accordingly, it would be beneficial to find additional methods to more easily remove oxygenates from olefins, particularly from an olefin stream synthesized from methanol

U.S. Patents Nos. 4,547,602 and 4,560,537 disclose a process for converting methanol to heavy hydrocarbons in the distillate range. In the first stage catalytic process, oxygenate is converted to lower olefins. The first stage effluent is cooled in an exchanger to condense water and a major amount of C5+ hydrocarbons. Byproduct water may be recovered from unreacted feedstock and discarded or a portion may be recycled.

U.S. Patent No. 4,387,263 discloses a process for making C2 to C4 olefins from gas mixtures containing methanol, dimethyl ether. The reaction gasses after condensation directs the reaction gasses and a condensed aqueous phase to a water scrubber in a water scrubbing column.

European Patent Application No. 0 060 103 discloses a process for converting methanol and/or dimethyl ether to a product containing ethylene. The product is condensed to form three phases—a liquid aqueous phase, a gaseous hydrocarbon phase and a liquid hydrocarbon phase. The liquid aqueous phase contains unreacted methanol and dimethyl ether. The liquid aqueous phase is stripped with low pressure steam to volatilize the methanol and/or dimethyl ether to from the aqueous phase. The methanol and/or dimethyl ether are recycled back to the reactor. Additionally, the gaseous hydrocarbon phase is contacted with methanol to selectively sorb unreacted dimethyl ether. An alternative contacts the gaseous phase with water to selectively remove dimethyl ether.

## Summary of the Invention

**[0004]** This invention provides a process for producing olefins from methanol such that oxygenate contaminants can be more easily removed from the olefin product. In one embodiment, the invention comprises a method for processing an olefin stream containing oxygenates (comprising organic compounds that contain at least one oxygen) and water. The method comprises providing an olefin stream containing oxygenates and water. The olefin stream is dewatered, and the dewatered olefin stream compressed. The compressed olefin stream is then washed with methanol to remove at least a portion of the oxygenate from the olefin stream. Following methanol wash, the olefin stream is contacted with water, and the water contacted olefin stream is fractionated.

[0005] In another embodiment, the water contacted olefin stream is dried prior to fractionating. In yet another embodiment, the washing of the olefin stream with the methanol and the water is carried out in a single wash column.

[0006] The invention also provides an embodiment, wherein the dewatered olefin stream is compressed to form a condensate containing dissolved heavy oxygenates and a gaseous olefin stream which is washed with the methanol. Desirably, the condensate is sent to a stripping column in which an overhead product of light hydrocarbons and a bottom product of C<sub>5</sub>+ hydrocarbons and heavy oxygenates are obtained. Preferably, the overhead product of light hydrocarbons is sent to at least one compression step.

In one embodiment, there is a method for producing olefins from methanol. According to the method, a molecular sieve catalyst is contacted with a first amount of methanol to produce an olefin stream. The olefin stream comprises an oxygenate. The oxygenate comprises an organic compound that contains at least one oxygen. The olefin stream is dewatered. The dewatered olefin stream is compressed. Then, the olefin stream is washed with a second amount of methanol to remove at least a portion of the oxygenate from the olefin stream. The second amount is from 1% to 10% of the first amount. Next, the methanol washed olefin stream is contacted with water. Thereafter, the water contacted olefin stream is fractionated.

**In another embodiment, the step of contacting a molecular sieve catalyst**



with a first amount of methanol occurs at a gas superficial velocity greater than 1 m/s. In another embodiment, the step of contacting converts from 90 wt.% to 98 wt.% of the first amount of methanol. In still another embodiment, the step of contacting converts above 98 wt.% to less than 100 wt.% of the first amount of methanol.

### Brief Description of the Drawing

[0007] The attached Figure shows an example of but one type of flow scheme of the invention in which methanol is used to remove undesirable oxygenates from an olefin stream synthesized from methanol.

## **Detailed Description of the Invention**

[0008] This invention provides a method for efficiently removing undesirable oxygenates from an olefin stream, particularly an olefin stream synthesized from methanol. The method is achieved in an economical way.

[0009] According to the invention, oxygenates are washed out of the gaseous olefin product stream after at least one compression step, and before the olefin product is dried. The oxygenates are washed out in a wash column with methanol.

[0010] The invention is based on the fact that the drying steps that are called for in conventional ethylene plants are not capable of handling more than very small amounts of oxygenates like aldehydes and ketones. Moreover, such oxygenates can polymerize under certain conditions, and the polymerization reactions can reduce the active surfaces of conventional drying schemes very rapidly. At present, there are no known dryers that are suitable for handling such components. For this reason, the oxygenates have to be removed from the product stream, before they enter the cold part of the processing plant, which consists of olefin drying and fractionation.

[0011] One conceivable possibility for removing the oxygenates would be to use all of the fresh methanol that is provided for olefin synthesis to wash the oxygenates out of the olefin product stream before the olefin synthesis. However, this would result in the olefin synthesis being loaded with reaction products from the olefin synthesis. This can lead to the accumulation of undesirable components.

[0012] In this invention, the olefin stream containing the oxygenate contaminants is quenched (dewatered), compressed and dried before fractionation. The oxygenate removal step is desirably performed after at least one compression step. If multiple compression steps are used, it is desirable that the oxygenate removal step be performed between the third and fourth compression step. It is also desired that the oxygenate removal step be performed after compression and before drying.

[0013] According to the invention, a wash column is provided for removing the oxygenate contaminant. Desirably, the oxygenates are washed out of the gaseous product stream with methanol in the wash column. Only a relatively small amount of methanol is needed for the oxygenate removal. For example, 1% to 10%, preferably 3% of the total amount of methanol used in the olefin synthesis, is used to wash out the oxygenates to an acceptable limit.

[0014] In another embodiment of the invention, overhead gas accumulating in the methanol wash is further washed with water. This removes methanol that may become entrained in the olefin stream as a result of evaporation in the preceding methanol wash. The gaseous product stream that is recovered from this water

wash contains, besides the olefins, only traces of oxygenates and methanol. The water washed olefin product stream is then sent to drying and fractionation.

[0015] In yet another embodiment of the invention, the water wash is carried out in an additional section of the wash column provided for the methanol wash. Desirably, a single wash column is provided for this, with the methanol wash being carried out in the lower part of the wash column, and the water wash in the upper part.

[0016] Another embodiment of the invention provides that the outlet pressure of at least one of the compression steps be adjusted so that, optionally after cooling, a hydrocarbon-containing condensate in which heavy oxygenates are dissolved is formed in addition to the gaseous product stream. The condensate can be sent to a stripping column, in which an overhead product of light hydrocarbons and a bottom product of  $C_5+$  hydrocarbons and heavy oxygenates is obtained. The overhead product of light hydrocarbons is desirably sent to at least one compression step. The bottom product of heavy hydrocarbons and oxygenates can be sent to further processing.

[0017] The invention provides an economical method for removing oxygenates from an olefin-containing product stream, and enables effective oxygen separation at very low investment cost. The invention is also advantageous in that only a very small amount of methanol is needed to remove the oxygenates from the olefin stream and that the wash stream can be used as feed to the olefin synthesis reactor. The olefin synthesis reaction will not be adversely affected by the methanol wash containing absorbed oxygenate. Nearly the same amount of fresh methanol is available for olefin synthesis. Desirably, the amount of methanol used in the methanol wash will be 1% to 10% of the total amount of the methanol that is used in the olefin synthesis reaction.

[0018] In one embodiment of the invention, the olefin product is obtained by contacting methanol with an olefin forming catalyst in a reactor. Preferably, the catalyst is a molecular sieve catalyst.

[0019] Although the use of methanol to produce the olefin stream is preferred, other oxygenate components can be used as a feed. Such oxygenates comprise at least one organic compound which contains at least one oxygen atom, such as

aliphatic alcohols, ethers, carbonyl compounds (aldehydes, ketones, carboxylic acids, carbonates, esters and the like). When the oxygenate is an alcohol, the alcohol includes an aliphatic moiety having from 1 to 10 carbon atoms, more preferably from 1 to 4 carbon atoms. Representative alcohols include but are not necessarily limited to lower straight and branched chain aliphatic alcohols and their unsaturated counterparts. Examples of suitable oxygenate compounds include, but are not limited to: methanol; ethanol; n-propanol; isopropanol; C<sub>4</sub>-C<sub>20</sub> alcohols; methyl ethyl ether; dimethyl ether; diethyl ether; di-isopropyl ether; formaldehyde; dimethyl carbonate; dimethyl ketone; acetic acid; and mixtures thereof. Dimethyl ether, or a mixture of dimethyl ether and methanol, are also preferred feeds.

[0020] Molecular sieves capable of converting an oxygenate such as methanol to an olefin compound include zeolites as well as non-zeolites, and are of the large, medium or small pore type. Small pore molecular sieves are preferred in one embodiment of this invention, however. As defined herein, small pore molecular sieves have a pore size of less than 50 nm (5.0 angstroms). Generally, suitable catalysts have a pore size ranging from 35 nm (3.5 angstroms) to 50 nm (5.0 angstroms), preferably from 40 nm (4.0 angstroms) to 50 nm (5.0 angstroms), and most preferably from 43 nm (4.3 angstroms) to 50 nm (5.0 angstroms).

[0021] Zeolite materials, both natural and synthetic, have been demonstrated to have catalytic properties for various types of hydrocarbon conversion processes. In addition, zeolite materials have been used as adsorbents, catalyst carriers for various types of hydrocarbon conversion processes, and other applications. Zeolites are complex crystalline aluminosilicates which form a network of AlO<sub>2</sub><sup>-</sup> and SiO<sub>2</sub> tetrahedra linked by shared oxygen atoms. The negativity of the tetrahedra is balanced by the inclusion of cations such as alkali or alkaline earth metal ions. In the manufacture of some zeolites, non-metallic cations, such as tetramethylammonium (TMA) or tetrapropylammonium (TPA), are present during synthesis. The interstitial spaces or channels formed by the crystalline network enable zeolites to be used as molecular sieves in separation processes, as catalyst for chemical reactions, and as catalyst carriers in a wide variety of hydrocarbon conversion processes.

[0022] Zeolites include materials containing silica and optionally alumina, and materials in which the silica and alumina portions have been replaced in whole or in part with other oxides. For example, germanium oxide, tin oxide, and mixtures thereof can replace the silica portion. Boron oxide, iron oxide, gallium oxide, indium oxide, and mixtures thereof can replace the alumina portion. Unless otherwise specified, the terms "zeolite" and "zeolite material" as used herein, shall mean not only materials containing silicon atoms and, optionally, aluminum atoms in the crystalline lattice structure thereof, but also materials which contain suitable replacement atoms for such silicon and aluminum atoms.

[0023] One type of olefin forming catalyst capable of producing large quantities of ethylene and propylene is a silicoaluminophosphate (SAPO) molecular sieve. Silicoaluminophosphate molecular sieves are generally classified as being microporous materials having 8, 10, or 12 membered ring structures. These ring structures can have an average pore size ranging from 35 nm (3.5 angstroms) to 150 nm (15 angstroms). Preferred are the small pore SAPO molecular sieves having an average pore size of less than 50 nm (5 angstroms), preferably an average pore size ranging from 35 nm (3.5 angstroms) to 50 nm (5 angstroms), more preferably from 35 nm (3.5 angstroms) to 42 nm (4.2 angstroms). These pore sizes are typical of molecular sieves having 8 membered rings.

[0024] According to one embodiment, substituted SAPOs can also be used in oxygenate to olefin reaction processes. These compounds are generally known as MeAPSOs or metal-containing silicoaluminophosphates. The metal can be alkali metal ions (Group IA), alkaline earth metal ions (Group IIA), rare earth ions (Group IIIB, including the lanthanoid elements: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium; and scandium or yttrium) and the additional transition cations of Groups IVB, VB, VIB, VIIB, VIIIB, and IB.

[0025] Preferably, the Me represents atoms such as Zn, Mg, Mn, Co, Ni, Ga, Fe, Ti, Zr, Ge, Sn, and Cr. These atoms can be inserted into the tetrahedral

framework through a  $[\text{MeO}_2]$  tetrahedral unit. The  $[\text{MeO}_2]$  tetrahedral unit carries a net electric charge depending on the valence state of the metal substituent.

When the metal component has a valence state of +2, +3, +4, +5, or +6, the net electric charge is between -2 and +2. Incorporation of the metal component is typically accomplished adding the metal component during synthesis of the molecular sieve. However, post-synthesis ion exchange can also be used. In post synthesis exchange, the metal component will introduce cations into ion-exchange positions at an open surface of the molecular sieve, not into the framework itself.

[0026] Suitable silicoaluminophosphate molecular sieves include SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44, SAPO-47, SAPO-56, the metal containing forms thereof, and mixtures thereof. Preferred are SAPO-18, SAPO-34, SAPO-35, SAPO-44, and SAPO-47, particularly SAPO-18 and SAPO-34, including the metal containing forms thereof, and mixtures thereof. As used herein, the term mixture is synonymous with combination and is considered a composition of matter having two or more components in varying proportions, regardless of their physical state.

[0027] An aluminophosphate (ALPO) molecular sieve can also be included in the catalyst composition. Aluminophosphate molecular sieves are crystalline microporous oxides which can have an  $AlPO_4$  framework. They can have additional elements within the framework, typically have uniform pore dimensions ranging from 30 nm (3 angstroms) to 100 nm (10 angstroms), and are capable of making size selective separations of molecular species. More than two dozen structure types have been reported, including zeolite topological analogues. A more detailed description of the background and synthesis of aluminophosphates is found in U.S. Pat. No. 4,310,440, which is incorporated herein by reference in its entirety. Preferred ALPO structures are ALPO-5, ALPO-11, ALPO-18, ALPO-31, ALPO-34, ALPO-36, ALPO-37, and ALPO-46.

[0028] The ALPOs can also include a metal substituent in its framework. Preferably, the metal is selected from the group consisting of magnesium, manganese, zinc, cobalt, and mixtures thereof. These materials preferably exhibit adsorption, ion-exchange and/or catalytic properties similar to aluminosilicate, aluminophosphate and silica aluminophosphate molecular sieve compositions.

Members of this class and their preparation are described in U.S. Pat. No.



4,567,029.

- [0029] The metal containing ALPOs have a three-dimensional microporous crystal framework structure of  $\text{MO}_2$ ,  $\text{AlO}_2$  and  $\text{PO}_2$  tetrahedral units. These as manufactured structures (which contain template prior to calcination) can be represented by empirical chemical composition, on an anhydrous basis, as:



wherein "R" represents at least one organic templating agent present in the intracrystalline pore system; "m" represents the moles of "R" present per mole of  $(\text{M}_x\text{Al}_y\text{P}_z)\text{O}_2$  and has a value of from zero to 0.3, the maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular metal aluminophosphate involved, "x", "y", and "z" represent the mole fractions of the metal "M", (i.e. magnesium, manganese, zinc and cobalt), aluminum and phosphorus, respectively, present as tetrahedral oxides.

- [0030] The metal containing ALPOs are sometimes referred to by the acronym as MeAPO. Also in those cases where the metal "Me" in the composition is magnesium, the acronym MAPO is applied to the composition. Similarly ZAPO, MnAPO and CoAPO are applied to the compositions which contain zinc, manganese and cobalt respectively. To identify the various structural species which make up each of the subgeneric classes MAPO, ZAPO, CoAPO and MnAPO, each species is assigned a number and is identified, for example, as ZAPO-5, MAPO-11, CoAPO-34 and so forth.

- [0031] The silicoaluminophosphate molecular sieve is typically admixed (i.e., blended) with other materials. When blended, the resulting composition is typically referred to as a SAPO catalyst, with the catalyst comprising the SAPO molecular sieve.

- [0032] Materials which can be blended with the molecular sieve can be various inert or catalytically active materials, or various binder materials. These materials include compositions such as kaolin and other clays, various forms of rare earth metals, metal oxides, other non-zeolite catalyst components, zeolite catalyst components, alumina or alumina sol, titania, zirconia, magnesia, thoria, beryllia, quartz, silica or silica sol, and mixtures thereof. These components are

also effective in reducing, inter alia, overall catalyst cost, acting as a thermal sink to assist in heat shielding the catalyst during regeneration, densifying the catalyst and increasing catalyst strength. It is particularly desirable that the inert materials that are used in the catalyst to act as a thermal sink have a heat capacity of from 0.05 to 1 cal/g-°C, more preferably from 0.1 to 0.8 cal/g-°C, most preferably from 0.1 to 0.5 cal/g-°C.

[0033] Additional molecular sieve materials can be included as a part of the SAPO catalyst composition or they can be used as separate molecular sieve catalysts in admixture with the SAPO catalyst if desired. Structural types of small pore molecular sieves that are suitable for use in this invention include AEI, AFT, APC, ATN, ATT, ATV, AWW, BIK, CAS, CHA, CHI, DAC, DDR, EDI, ERI, GOO, KFI, LEV, LOV, LTA, MON, PAU, PHI, RHO, ROG, THO, and substituted forms thereof. Structural types of medium pore molecular sieves that are suitable for use in this invention include MFI, MEL, MTW, EUO, MTT, HEU, FER, AFO, AEL, TON, and substituted forms thereof. These small and medium pore molecular sieves are described in greater detail in the *Atlas of Zeolite Structural Types*, W.M. Meier and D.H. Olsen, Butterworth Heineman, 3rd ed., 1997, the detailed description of which is explicitly incorporated herein by reference. Preferred molecular sieves which can be combined with a silicoaluminophosphate catalyst include ZSM-5, ZSM-34, erionite, and chabazite.

[0034] The catalyst composition, according to an embodiment, preferably, comprises from 1% to 99 %, more preferably from 5 % to 90 %, and most preferably from 10% to 80%, by weight of molecular sieve. It is also preferred that the catalyst composition have a particle size of from 0.2µm (20 angstroms) to 30 µm (3,000 angstroms), more preferably from 0.3 µm (30 angstroms) to 2 µm (200 angstroms), most preferably from 0.5 µm (50 angstroms) to 1.5 µm (150 angstroms).

[0035] The catalyst can be subjected to a variety of treatments to achieve the desired physical and chemical characteristics. Such treatments include, but are not

necessarily limited to hydrothermal treatment, calcination, acid treatment, base treatment, milling, ball milling, grinding, spray drying, and combinations thereof.

[0036] A molecular sieve catalyst particularly useful in making ethylene and

propylene is a catalyst which contains a combination of SAPO-34, and SAPO-18 or ALPO-18 molecular sieve. In a particular embodiment, the molecular sieve is a crystalline intergrowth of SAPO-34, and SAPO-18 or ALPO-18.

**[0037]** To convert methanol or other oxygenate to olefin, conventional reactor systems can be used, including fixed bed, fluid bed or moving bed systems. Preferred reactors of one embodiment are co-current riser reactors and short contact time, countercurrent free-fall reactors. Desirably, the reactor is one in which an oxygenate feedstock can be contacted with a molecular sieve catalyst at a weight hourly space velocity (WHSV) of at least  $1 \text{ hr}^{-1}$ , preferably in the range of from  $1 \text{ hr}^{-1}$  to  $1000 \text{ hr}^{-1}$ , more preferably in the range of from  $20 \text{ hr}^{-1}$  to  $1000 \text{ hr}^{-1}$ , and most preferably in the range of from  $50 \text{ hr}^{-1}$  to  $500 \text{ hr}^{-1}$ . WHSV is defined herein as the weight of oxygenate, and reactive hydrocarbon which may optionally be in the feed, per hour per weight of the molecular sieve in the reactor. Because the catalyst or the feedstock may contain other materials which act as inerts or diluents, the WHSV is calculated on the weight basis of the oxygenate feed, and any reactive hydrocarbon which may be present with the oxygenate feed, and the molecular sieve contained in the reactor.

**[0038]** Preferably, the oxygenate feed is contacted with the catalyst when the oxygenate is in a vapor phase. Alternately, the process may be carried out in a liquid or a mixed vapor/liquid phase. When the process is carried out in a liquid phase or a mixed vapor/liquid phase, different conversions and selectivities of feed-to-product may result depending upon the catalyst and reaction conditions.

**[0039]** The process can generally be carried out at a wide range of temperatures. An effective operating temperature range can be from  $200^{\circ}\text{C}$  to  $700^{\circ}\text{C}$ , preferably from  $300^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ , more preferably from  $350^{\circ}\text{C}$  to  $550^{\circ}\text{C}$ . At the lower end of the temperature range, the formation of the desired olefin products may become markedly slow with a relatively high content of oxygenated olefin by-products being found in the olefin product. However, the selectivity to ethylene and propylene at reduced temperatures may be increased. At the upper end of the temperature range, the process may not form an optimum amount of ethylene and propylene product, but the conversion of

oxygenate feed will generally be high.

**[0040]** Operating pressure also may vary over a wide range, including autogenous pressures. Effective pressures include, but are not necessarily limited to, a total pressure of at least 1 psia (7 kPa), preferably at least 5 psia (34 kPa). The process is particularly effective at higher total pressures, including a total pressure of at least 20 psia (138 kPa). Preferably, the total pressure is at least 25 psia (172 kPa), more preferably at least 30 psia (207 kPa). For practical design purposes it is desirable to use methanol as the primary oxygenate feed component, and operate the reactor at a pressure of not greater than 500 psia (3445 kPa), preferably not greater than 400 psia (2756 kPa), most preferably not greater than 300 psia (2067 kPa).

**[0041]** Undesirable by-products can be avoided by operating at an appropriate gas superficial velocity. As the gas superficial velocity increases the conversion decreases avoiding undesirable by-products. As used herein, the term, "gas superficial velocity" is defined as the combined volumetric flow rate of vaporized feedstock, which includes diluent when present in the feedstock, as well as conversion products, divided by the cross-sectional area of the reaction zone. Because the oxygenate is converted to a product having significant quantities of ethylene and propylene while flowing through the reaction zone, the gas superficial velocity may vary at different locations within the reaction zone. The degree of variation depends on the total number of moles of gas present and the cross section of a particular location in the reaction zone, temperature, pressure and other relevant reaction parameters.

**[0042]** In one embodiment, the gas superficial velocity is maintained at a rate of greater than 1 meter per second (m/s) at least one point in the reaction zone. In another embodiment, it is desirable that the gas superficial velocity is greater than 2 m/s at least one point in the reaction zone. More desirably, the gas superficial velocity is greater than 2.5 m/s at least one point in the reaction zone. Even more desirably, the gas superficial velocity is greater than 4 m/s at least one point in the reaction zone. Most desirably, the gas superficial velocity is greater than 8 m/s at least one point in the reaction zone.

**[0043]** According to yet another embodiment of the invention, the gas superficial

velocity is maintained relatively constant in the reaction zone such that the gas superficial velocity is maintained at a rate greater than 1 m/s at all points in the reaction zone. It is also desirable that the gas superficial velocity be greater than 2 m/s at all points in the reaction zone. More desirably, the gas superficial velocity is greater than 2.5 m/s at all points in the reaction zone. Even more desirably, the gas superficial velocity is greater than 4 m/s at all points in the reaction zone. Most desirably, the gas superficial velocity is greater than 8 m/s at all points in the reaction zone.

[0044] The amount of ethylene and propylene produced in the oxygenate to olefin process can be increased by reducing the conversion of the oxygenates in the oxygenate to olefins reaction. However, reducing the conversion of feed oxygenates in the oxygenate conversion reaction tends to increase the amount of oxygenated hydrocarbons, particularly including dimethyl ether, that are present in the olefin product. Thus, control of the conversion of feed to the oxygenate reaction process can be important.

[0045] According to one embodiment, the conversion of the primary oxygenate, e.g., methanol, is from 90 wt % to 98 wt %. According to another embodiment the conversion of methanol is from 92 wt % to 98 wt %, preferably from 94 wt % to 98 wt %.

[0046] According to another embodiment, the conversion of methanol is above 98 wt % to less than 100 wt %. According to another embodiment, the conversion of methanol is from 98.1 wt % to less than 100 wt %; preferably from 98.2 wt % to 99.8 wt %. According to another embodiment, the conversion of methanol is from 98.2 wt % to less than 99.5 wt %; preferably from 98.2 wt % to 99 wt %.

[0047] In this invention, weight percent conversion is calculated on a water free basis unless otherwise specified. Weight percent conversion on a water free basis is calculated as:  $100 \times (\text{weight oxygenate fed on a water free basis} - \text{weight oxygenated hydrocarbon in the product on a water free basis})$ . The water free basis of oxygenate is calculated by subtracting out the water portion of the oxygenate in the feed and product, and excluding water formed in the product. For example, the weight flow rate of methanol on an oxygenate free basis is calculated by multiplying the weight flow rate of methanol by 14/32 to remove the

which can contain evaporated methanol from the methanol wash is contacted with fresh water, which is sent to the wash column 12 via a pipe 16. The overhead gas exiting the upper part 14 of the wash column 12 contains only tolerable traces of oxygenates and methanol.

[0053] The overhead gas exiting the upper part 14 is sent via a pipe 17. This gas can be sent, for example, to an alkali wash and to a drying step. Then fractionation of the olefin (not shown in the Figure) is carried out.

[0054] The bottom product of the water wash is sent partly through the lower part 13 of the wash column 12, and partly to a flash drum 20 as by-pass via a pipe 19. The gas accumulating in flash drum 20 contains predominantly ethylene and propylene, and is sent back to the process via the compression steps. The liquid accumulating in flash drum 20 is a methanol-water solution that contains the oxygenates in a high concentration. This liquid is removed via a pipe 22, and can be sent to incineration or otherwise utilized. Alternatively, this solution can be sent to a methanol-water distillation separation, where the oxygenates remain in the distillate. The solution can also be returned to the process together with the methanol. Through other separation steps, it is also possible to obtain clean methanol and to discard the oxygenate. In the case of a light waste gas, it may be meaningful to choose the pressure in pipe 1 after the compression steps so that no hydrocarbon condensate accumulates. In this case, the three-phase separator 4 and the stripping column 5 can be omitted.

**What is claimed is:**

1. A method for processing an olefin stream containing oxygenates and water, wherein the oxygenates comprise organic compounds that contain at least one oxygen, comprising:
  - providing an olefin stream containing oxygenates and water;
  - dewatering the olefin stream;
  - compressing the dewatered olefin stream;
  - washing the olefin stream with methanol to remove at least a portion of the oxygenate from the olefin stream;
  - contacting the methanol washed olefin stream with water; and
  - fractionating the water contacted olefin stream.
2. The method of claim 1, further comprising drying the water contacted olefin stream prior to fractionating.
3. The method of claim 1, wherein the washing the olefin stream with methanol to remove at least a portion of the oxygenate from the olefin stream; and the contacting the methanol washed olefin stream with water is carried out in a single wash column.
4. The method of claim 1, wherein the dewatered olefin stream is compressed to form a condensate containing dissolved heavy oxygenates and a gaseous olefin stream which is washed with the methanol.
5. The method of claim 4, further comprising sending the condensate to a stripping column in which an overhead product of light hydrocarbons and a bottom product of C<sub>5</sub>+ hydrocarbons and heavy oxygenates are obtained.
6. The method of claim 5, wherein the overhead product of light hydrocarbons is sent to at least one compression step.



7. A method for producing olefins from methanol, the method comprises the steps of:

contacting a molecular sieve catalyst with a first amount of methanol to produce an olefin stream, comprising an oxygenate wherein the oxygenate comprises an organic compound that contains at least one oxygen;

dewatering the olefin stream;

compressing the dewatered olefin stream;

washing the olefin stream with a second amount of methanol to remove at least a portion of the oxygenate from the olefin stream, wherein the second amount is from 1% to 10% of the first amount;

contacting the methanol washed olefin stream with water; and

fractionating the water contacted olefin stream.

8. The method of claim 7, further comprising drying the water contacted olefin stream prior to fractionating.

9. The method of claim 7, wherein the washing the olefin stream with methanol to remove at least a portion of the oxygenate from the olefin stream; and the contacting the methanol washed olefin stream with water is carried out in a single wash column.

10. The method of claim 7, wherein the dewatered olefin stream is compressed to form a condensate containing dissolved heavy oxygenates and a gaseous olefin stream which is washed with the methanol.

11. The method of claim 10, further comprising sending the condensate to a stripping column in which an overhead product of light hydrocarbons and a bottom product of C<sub>5</sub>+ hydrocarbons and heavy oxygenates are obtained.

12. The method of claim 11, wherein the overhead product of light hydrocarbons is sent to at least one compression step.

13. The process of claim 7, wherein the step of contacting the molecular sieve catalyst occurs at a gas superficial velocity greater than 1 m/s.

14. The process of claim 7, wherein the step of contacting the molecular sieve catalyst converts from 90 wt.% to 98 wt.% of the first amount of methanol.

15. The process of claim 7, wherein the step of contacting converts above 98 wt.% to less than 100 wt.% of the first amount of methanol.